Direct imaging through scattering media by use of efficient third-harmonic generation in organic materials

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Received May 24, 2004

We report on real-time, time-gated, direct imaging through scattering media with an attenuation of 14 mean-free paths by use of third-harmonic generation in the eye-safe and telecommunication-compatible near-IR spectral region (1550 nm). © 2004 Optical Society of America

OCIS codes: 190.2620, 290.7050, 190.4710.

Nonlinear optical processes can convert laser beams at frequency ω into beams at higher harmonic frequencies.[1] Second-harmonic generation, a process in which a beam is produced at frequency 2ω, is the lowest-order nonlinear process and the most efficient. It has found applications in a wide range of fields, including material and interface characterization,[2] laser frequency conversion,[1] short laser pulse diagnostics,[3] and microscopy and imaging.[4] Although second-harmonic generation is limited to materials or interfaces that lack inversion symmetry, third-harmonic generation (THG), which produces a beam at 3ω, can in principle be observed in any isotropic bulk material. To date, applications of THG have been limited by a paucity of materials that generate strong THG radiation. Since third-order nonlinear optical susceptibilities are orders of magnitude lower than second-order ones, high-intensity lasers are required for production of significant THG intensities. Fortunately, ultrafast lasers have gained in power and portability in recent years, especially lasers that emit in the near IR at telecommunication wavelengths. Such lasers are simultaneously eye safe and used in lidar systems. Therefore it is important to develop materials that can produce strong THG signals from lasers that emit in the 1300–1800-nm range.

THG signals that are readily visible to the naked eye in a well-lit room were first observed from 10-μm-thick films of polystyrene containing 20 wt.% of the molecule E-2-tricyanovinyl-3-n-hexyl-5-[4-bis(4-n-butylphenyl)amino-2-methoxy-styryl]thiophene (molecule 1 in Fig. 1) when the films were placed at the focus of a pulsed laser beam with a wavelength of 1550 nm produced by an optical parametric oscillator pumped by a Ti:sapphire laser with a pulse width of 95 fs and a repetition rate of 82 MHz. At the maximum pump power of 250 mW, a third-harmonic signal of 17 μW was generated and a third-order susceptibility tensor element of $\chi_{zzzz}^{(3)} = 8.2 \times 10^{-20}$ (m/V)^2 (5.8×10^{-12} esu) was calculated. From the dispersion of the linear refractive index evaluated for these films, we observed that the THG process was not phase matched. As a result, the THG process is not very sensitive to the wavelength of the fundamental radiation and has a broad spectral bandwidth, as illustrated in Fig. 1. For these measurements the fundamental wavelength was scanned by a β-barium borate OPO pumped by the third harmonic of a Q-switched Nd:YAG laser (Spectron SL802G). Using THG in these films, we developed third-order autocorrelation[5]

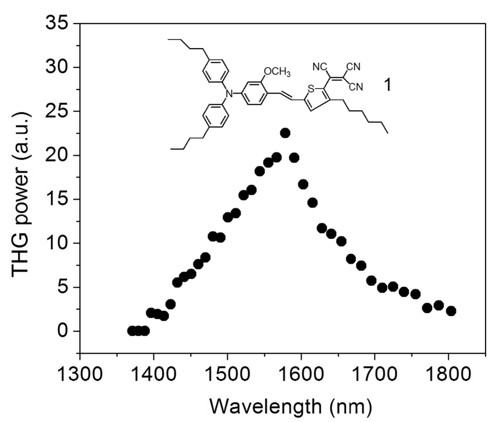

Fig. 1. Intensity of the THG signal as a function of the wavelength of the fundamental beam. Inset, chemical structure of the nonlinear chromophore.

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and frequency-resolved optical gating techniques for characterization of short pulses.[6] These strong THG signals encouraged us to explore the use of these materials for image reconstruction in scattering media.

Recently, imaging through scattering media by use of nonlinear optical processes[7] has attracted considerable attention because of its importance in medical diagnosis and in applications requiring the propagation of short pulses in a turbid atmosphere. The key to successful imaging under these conditions is to separate the unscattered ballistic photons from the background scattered light that completely blurs the image. Because ballistic photons emerge from a scattering medium before the diffusive photons, filtering of the image can be implemented by using several ultrafast time-gating techniques.[8–13] All these techniques have their advantages and limitations.

The use of THG as an incoherent time-gating imaging technique described here combines the following attributes: (i) it is a nonscanning direct imaging technique with a response time limited by the duration of the short pulses that are used; (ii) it has high sensitivity because the ballistic photons are amplified during the nonlinear frequency conversion process by the reference pulse; (iii) the non-phase-matched nature of the process provides a large spectral and angular bandwidth; (iv) samples can be fabricated at low cost into rugged objects of various shapes and thicknesses by use of standard coating and molding processes; and (v) imaging is demonstrated in the near IR in the eye-safe region and at telecommunication wavelengths, and the frequency-upconverted signals (visible) can be detected with low-cost Si photodiodes.

To illustrate these attributes we performed $4f$ Fourier imaging experiments in the noncollinear geometry shown in Fig. 2 with our optical parametric oscillator system. In this geometry two beams (object and reference beams) at frequency ω produce four beams at frequency 3ω when they overlap temporally in the sample. As shown in Fig. 2, these beams propagate in directions $3\mathbf{k}_1$, $2\mathbf{k}_1 + \mathbf{k}_2$, $2\mathbf{k}_2 + \mathbf{k}_1$, $3\mathbf{k}_2$, where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave vectors of the reference and the object beams, respectively. They describe four different ways to produce a signal at frequency 3ω. Of particular interest for imaging is the beam propagating in the $2\mathbf{k}_1 + \mathbf{k}_2$ direction, for which the amplitude of the field at frequency 3ω, $E_s(r,t)$ is, to a good approximation, proportional to the product $E_2(r,t)E_1{}^2(r,t)$, where $E_2(r,t)$ and $E_1(r,t)$ are the field amplitudes of the object and the reference beams, respectively. Time gating in this case is achieved by adjusting the delay of the reference pulse so that it overlaps the ballistic photons in the object beam and converts them into a signal at frequency 3ω. Note that delayed scattered photons from the object beam propagating in the $\mathbf{k}_2$ direction contribute to the THG signal that is propagating in the $3\mathbf{k}_2$ direction. This shows that noncollinear THG simultaneously provides a means to filter the signal temporally and spatially. For these experiments we used 10-μm-thick films of a polymer composite containing 20 wt. % of molecule 1 and 80 wt. % of polystyrene. Samples were prepared in air by melting the polymer composite between two glass slides on a hot plate at 170 °C. The thickness of the sample was controlled by calibrated spacers. The objects were printed on transparencies and placed into the object beam as shown in Fig. 2. As an example, we used the numeral 4 as an object whose spatial Fourier components were imaged onto the organic sample. The numeral 4 was chosen from other numerals because it is the most difficult to image with good integrity because of a wide spread of its spatial frequencies in the Fourier plane. The reference pulse was focused to a relatively large spot to overlap all the Fourier components. To image under scattering conditions we introduced a 1-cm-thick cell containing suspensions of silica microspheres in deuterated water into the path of the object beam. The scattering conditions at 1550 nm were varied by increasing the concentration of microspheres to an attenuation of up to nine mean-free paths, equivalent to an optical density (O.D.) of 4. For reference, the object beam at the fundamental IR frequency was imaged independently with an IR-sensitive detector array. A first example of image filtering is shown in Fig. 3. The nonfiltered images of the numeral 4 detected with an IR camera at the fundamental wavelength of 1550 nm are shown in the top row after propagation in scattering media with increasing attenuation. For scattering conditions of O.D. larger than 3, the object is completely blurred by noise. In contrast, the filtered images shown in

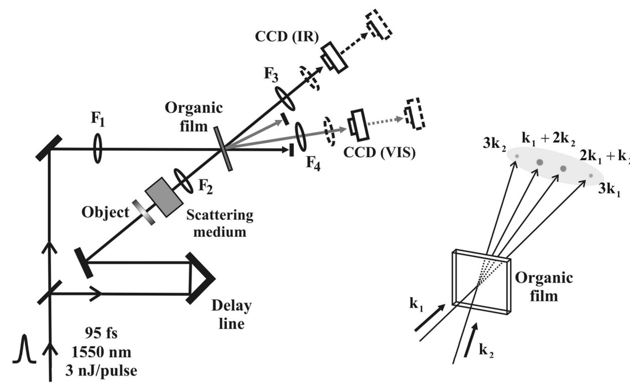

Fig. 2. Setup for the imaging experiments through scattering media. The dotted lines indicate the positions of the lenses and cameras used to image the Fourier spectrum of a plane wave (with no object present in the setup). The right-hand side of the figure presents a wave-vector construction for noncollinear THG.

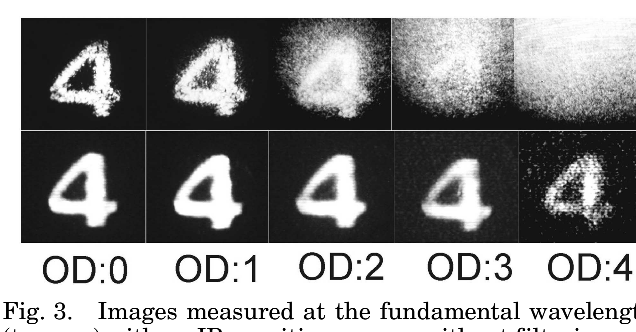

Fig. 3. Images measured at the fundamental wavelength (top row) with an IR-sensitive camera without filtering and images measured at the third harmonic (bottom row) in the direction $2\mathbf{k}_1 + \mathbf{k}_2$, after propagation in scattering media with increasing O.D.

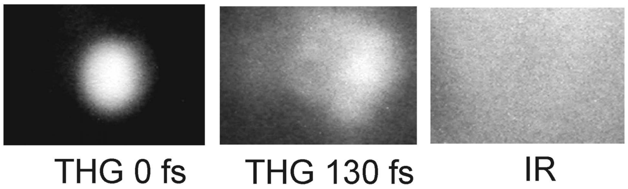

Fig. 4. THG intensity of the central lobe of the Fourier spectrum of a plane wave imaged in the $2\mathbf{k}_1 + \mathbf{k}_2$ direction at temporal overlap (left) and for a delay of 130 fs between the two pulses after propagation in a medium with an O.D. of 6 (center); unfiltered image at the fundamental wavelength detected with an IR-sensitive camera (right).

the bottom row of Fig. 3 at the third harmonic are clearly visible. The quality of the image is limited by the electronic noise of the low-cost CCD array. To illustrate that higher sensitivity can be achieved, we removed the object and imaged the Fourier spectrum of a plane wave going through a scattering medium. This provided a higher photon density for the camera. As shown in Fig. 4, in this case the central lobe of the Fourier spectrum can be clearly reconstructed with the THG signal for scattering conditions of up to an O.D. of 6, corresponding to 14 mean-free paths. Also shown in Fig. 4 is the THG signal when a delay of 130 fs is introduced between the two beams. The quality of the image rapidly degrades.

These results suggest that noncollinear THG provides a promising time-gating technique for imaging through scattering media. Direct imaging under 14-mean-free-path attenuation has been demonstrated with low-cost detectors, but the technique has the potential to provide much higher sensitivity if high-performance cameras and image processing techniques are used. The spectral properties of these organic materials and the non-phase-matched nature of the THG process allow for their use with pulsed lasers that emit in the 1400–1800-nm spectral range. Efficient THG process in this spectral region is of considerable technological interest because it overlaps the telecommunication wavelengths and coincides with eye-safe lasers used, for instance, in lidar applications. To further improve the technique presented here, mainly its sensibility, there is a need for synthesizing chromophores with higher nonlinearity and lower absorption at 3ω.

This material is based on work supported in part by the Science and Technology Centers Program of the National Science Foundation under agreement DMR-0120967, by the Defense Advanced Research Projects Agency, by the U.S. Air Force Office of Scientific Research, by a National Science Foundation CAREER program [B. Kippelen, to whom correspondence may be addressed (kippelen@ece.gatech.edu)], and by the Consejo Nacional de Ciencia y Technología. M. Cha acknowledges support from a Korea Research Foundation Grant (KRF-2001-013-D00037).

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